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CONTROL AND MITIGATION SYSTEMS FOR ACCIDENTAL RELEASES OF TOXIC CHEMICALS

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16. ABSTRACT The paper discusses control and mitigation systems for accidental releases of toxic chemicals. A review of the control/mitigation system data base developed during an EPA study reveals that the major control measure employed by industry for accidental releases is routine process inspections. For control devices, flares and scrubbers were found to be the control systems of choice for handling such releases. The types of accidental release control systems appear to be chemical-specific, although insufficient data were available per chemical to establish trends for different chemicals. For hydrogen sulfide and hydrogen cyanide, flares seem to be the preferred control device in industry for accidental releases. The mitigation systems data base revealed a variety of techniques (e.g., water misting, dikes, foam covers) in industry for limiting the spread of an accidental release. The limited data base did not allow any clear trends to be established for mitigation systems by type of chemical. The control/mitigation system data base also pointed out that companies viewed improved inspections and equipment testing as the best way to prevent accidental releases.

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INTRODUCTION

Concern regarding potential releases of acute toxic chemicals has been heightened considerably since the tragic incident in Bhopal, India, on December 3, 1984, when the release of an estimated 36 metric tons of methyl isocyanate from a storage vessel at a chemical plant resulted in the deaths of over 2,000 people. In the United States, the Environmental Protection Agency (EPA) has formed an Acute Hazards List Workgroup to establish a list of acutely hazardous chemicals and investigate the safety-related characteristics of the U.S. industry with respect to accidental chemical releases.

In June 1985, EPA announced a revised national strategy to reduce the risks posed by hazardous air pollutants (HAPs). The new strategy included measures to deal with accidental releases of toxic chemicals and to enhance enforcement of the air toxics control program under the Clean Air Act, the Toxic Substances Control Act, the Resource Conservation and Recovery Act, and the Clean Water Act. To aid in planning both the prevention of accidental releases of hazardous substances and the conduct of timely and effective emergency response in the event of such releases, as part of the new strategy EPA subsequently initiated the Chemical Emergency Preparedness Program (CEPP). This voluntary program has two goals: 1) to increase community awareness of potential chemical hazards, and 2) to stimulate the development of State and local emergency response plans for dealing with chemical accidents.[1]

To gain insight into the factors involved in accidental releases of hazardous substances, EPA also developed under CEPP a computerized Acute Hazardous Events (AHE) data base,[2] which catalogs information on the causes and results of thousands of such releases that have occurred in the U.S. from 1980 to 1985. The AHE data base identifies trends for accidental releases with respect to chemicals released, industries affected, in-plant sources of release, causative factors, and emergency procedures undertaken for remediation. As a follow-up to the AHE data base, PEI Associates, Inc. has developed for EPA's Office of Toxic Substances a separate Regional Office (RO) data base on accidental chemical industry releases based on information

obtained from five EPA ROs (Regions 2, 4, 5, 6, and 7). Neither data base, however, comprehensively characterizes the control and mitigation systems associated with accidental release conditions. Such information would be useful for transferring knowledge throughout industry on practices for accidental release prevention.

Under contract to EPA's Air and Energy Engineering Research Laboratory (AEERL), PEI conducted an evaluation of the current usage in industry of control and mitigation systems for accidental releases of various toxic chemicals. The study goal was accomplished through a review of data obtainable from plant inspections for emergency preparedness conducted in the recent past by EPA, the Occupational Safety and Health Administration (OSHA), the National Institute for Chemical Studies (NICS),[3] and other agencies. Very little coordination exists between the different groups that have conducted such inspections. The primary objective of the study was to analyze and summarize basic trends on control and mitigation practices in industry based on plant inspection data collected from the various sources. A secondary objective was to analyze any other basic trends (e.g., citations, preventive measures) that could be learned from this review. This paper focuses on the results of this study.

CONTROL AND MITIGATION TECHNOLOGIES

Whenever chemicals are handled or processed, there exists the potential for accidental release. Release of an acutely toxic chemical can result in an unacceptable risk to property, to the public, and to the environment. The chemical industry uses emission control systems to minimize this risk by reducing the volume of the unforeseen release, and mitigation systems to limit the spread of the release.

Control devices employ one of two principles: combustion or recovery. Combustion-type control devices include thermal incinerators, catalytic incinerators, flares, and boilers/process heaters. Examples of recovery-type control devices include condensers, adsorbers, and absorbers. The applicability of a specific control device depends on the chemical being handled in a given process.

Two general methods of mitigating a given release are used in industry: reduction of the concentration of a contaminant, and physical containment of the released chemical. These methods may be used separately or in conjunction with each other. The concentration of a contaminant can be reduced using techniques such as water sprays, water curtains, and chemical neutralization. Physical containment can be effected by devices such as dikes or covers.

Control Devices

Thermal incinerators are generally not suitable for accidental releases because of their relatively limited turndown ratios. Reduced residence time and poor mixing during increased flow conditions decrease the completeness of destruction.[4] Holding tanks or gas holders, however, can be used to provide a controlled flow to the incinerator, aiding combustion. In thermal incineration systems, the concentration of the emitted volatile organic compound (VOC) to be treated is generally limited to 25 percent of its LEL (lower explosive limit); therefore, if the concentration is high, dilution air may be required.[4] For routine process emissions, a thermal incinerator can achieve HAP destruction efficiencies of greater than 99 percent.[4]

For reasons similar to those described above for thermal incinerators, catalytic incinerators are not generally used under accidental release conditions. In addition, materials such as phosphates, halogens, and sulfur can effectively poison a catalyst, thereby adversely affecting incinerator performance. Liquid or solid particles that may deposit on the catalyst surface can also reduce the destruction efficiency of catalytic incinerators. Optimally, HAP destruction efficiencies of up to 95 percent can be achieved using catalytic incinerators.[4]

Flares are usually provided to burn combustible materials vented during start-up, shutdown, or emergency conditions. Flares are the combustion control devices of choice for accidental release conditions. A flare system consists of a stack with pilot flames at the tip. An ignitor is provided to re-light the pilot when it goes out. Headers collect the gases or vapors to be vented. Steam-assisted flares are typically used for combustion of large-volume releases. Generally, steam-assisted flares will only prevent smoking up to about 30 percent of flame capacity. Thus, smoking may occur under full, emergency releases. Auxiliary fuel may be required if the emission stream does not have sufficient heating value. The flare should be of sufficient height to prevent dangerous ground-level vapor concentrations if the flare is extinguished. The feed header should be purged continuously with an inert gas or non-condensible fuel to prevent air from entering the stack. Optimally, a flare system can achieve greater than 98 percent HAP destruction efficiencies.[4]

Boilers/process heaters are generally not suitable for accidental releases for reasons similar to those described for thermal incinerators.

Condensers are recovery-type control devices that reduce vapor emissions from leaking equipment by cooling the vapor below the dew point and recovering the condensate. Water is generally used as the cooling medium for chemicals having relatively high boiling points. Refrigerants are necessary for low-boiling point chemicals. Condensers are frequently used as preliminary air pollution control devices for reducing VOC emissions prior to treatment by incinerators, adsorbers, or absorbers.[4] The removal efficiencies of condensers range between 50 and 90 percent depending on the characteristics of the HAP released.[4]

Adsorption, usually through use of a carbon medium, is suitable for handling low-volume or low-concentration emissions. Inlet concentrations above 1,000 ppmv may not be adequately handled due to limitations on the

adsorptive capacity of the medium. Outlet concentrations of 100 ppmv can be achieved routinely. High bed temperatures resulting from heat of adsorption can cause vapors to ignite, posing a safety hazard. Excessive temperatures in the bed can be reduced by dilution or condensation of the emission stream prior to adsorption. The presence of liquids, solids, or polymerizable monomers may reduce the effectiveness of the adsorption column by clogging active sites. Optimally, 95 to 99 percent HAP removal efficiencies can be achieved by carbon adsorption.[4] Adsorption efficiencies greater than 99 percent have been reported for hydrogen fluoride and hydrogen sulfide using calcined alumina and ammonia-impregnated activated carbon, respectively.[4]

Absorbers (or scrubbers) are more commonly used as control devices for inorganic vapor emissions (e.g., ammonia, chlorine) than for organic vapor emissions.[4] A scrubber provides a good contact surface for dissolving a vapor into a liquid. Water is used to absorb soluble vapors, whereas caustic solutions are used to remove chlorine and acid vapors. Vapor/liquid data are required to adequately design an absorber system. Accidental release flows that are large can cause severe temperature rises and control device breakthrough.[5] The liquid used for absorption must be disposed of as a waste. Optimally, HAP removal efficiencies greater than 99 percent can be achieved through absorption.[4]

It could not be determined from the literature review if all of the aforementioned control devices are used for accidental releases.

Mitigation Devices

Water sprays can be used to mitigate water-soluble chemical emissions.[5] The contaminated water is usually sent to holding tanks where the liquid can be removed for disposal or sent to waste treatment. Water sprays can also dilute vapor clouds by mixing the released vapor with air entrained in the water spray. Hand-held nozzle sprays can be used to move vapor clouds away from ignition sources.

If sources of high potential leakage can be identified, a "curtain" of water-fog sprays can mitigate emissions. Water curtains act primarily as dilution devices, mixing the release with entrained air. Very soluble chemicals (e.g., acid vapors), however, can be absorbed. Curtains can be manually or automatically activated when concentrations approach safety limits. Water curtains are only marginally effective in reducing the effects of water-insoluble chemicals.[5] Air entrained by the curtain can become contaminated because of dense vapor flow over and/or around the curtain. High winds can decrease the effectiveness of the curtain. Generally, water curtains are used to mitigate water-soluble, low density, or non-flammable vapors.

A vapor or volatile liquid can be reacted with another material (neutralizing agent) to form a less-toxic and/or less-volatile liquid or solid. The neutralizing agent, however, must be available in sufficient quantities to handle the release. Soda ash, limestone, or weak caustic soda solutions may be used for acidic spills.[5] Fire-extinguishing equipment has recently

been adapted to apply the agent from a distance. The solid or liquid resulting from neutralization must be properly disposed of in landfills.

Liquid spills can be physically contained by dikes. The purpose of a diking system is to limit the spread of liquid from the immediate spill area to other plant areas or to areas outside the plant.[6] Dikes can be either permanently installed or temporarily constructed at the time of the spill. Curbing must be high enough to hold a given spill before vacuuming to holding tanks or discharging to a treatment system via trenches.

Covering materials can be applied to liquid spills to reduce vaporization. Covers can be liquids, foams, or solids. Liquids used as covers must be immiscible and non-reactive with the spilled volatile. For example, bromine and carbon disulfide can be effectively covered with water.[5] Foams can be effective vapor suppressants and are commonly used to prevent rapid evaporation from liquid spills.[7] Foams are used to cover hydrocarbons and alkaline or acidic liquids. Metal stearate foams have been used to mitigate spills of organic polar compounds.[8] Foam covers, 10 to 15 centimeters deep, can reduce the volatilization rates of liquid spills by greater than 40 percent.[5] Solid covers such as sand, sulfate powders, or polymer beads can reduce vaporization rates by reducing the area exposed to the air. A non-reactive solid material less dense than the spilled liquid is typically used. If the spill is not very deep, adsorbent materials can be used to remove the spill material and reduce the vaporization potential. Cover materials are intended to cover confined liquid spills (e.g., in dikes), and are not effective on running spills.

DATA BASES

To better establish the methods that are currently used in industry to control and mitigate accidental releases, PEI contacted various government and private organizations/study groups to determine the availability of data bases that may provide information on control and mitigation practices. During this research, the following organizations/study groups provided information: 1) EPA Region 6; 2) OSHA; and 3) NICS.

EPA Region 6

Most of the information obtained by PEI for this study was through Region 6's Technical Assistance Team (TAT) emergency response/removal action reports. These reports present information from site investigations conducted from 1985 to 1987 following accidental releases at plants within the Region. Information on the circumstances behind an individual accidental release was gathered by the TAT groups through discussions with plant environmental officials. The TAT reports mainly focus on accidental release notification procedures, the cause of the release, and effects of the release. Information on control/mitigation systems in place at the time of the accident, however, is also provided in many of the reports.

OSHA

In 1986, OSHA conducted a Chemical Special Emphasis Program (ChemSEP) of in-depth safety inspections for the chemical industry.[9] Unlike ordinary OSHA inspections which focus on physical facilities and health hazards, ChemSEP evaluated safety and health management, including emergency preparedness.

Under ChemSEP, OSHA visited 40 chemical plants. One process unit, which manufactured 1 of OSHA's 10 targeted chemicals under ChemSEP (acetylene, phosgene, chlorine, hydrogen sulfide, hydrogen, ammonia, hydrogen selenide, acrylonitrile, formaldehyde, and bis-chloromethyl ether) was inspected at each plant. Each inspection averaged more than 383 inspector-hours.[9] ChemSEP inspections included a broad cross-section of standard industrial classification (SIC) codes and plant capacities. ChemSEP inspections were conducted in seven states: Louisiana, New Jersey, New York, Ohio, Pennsylvania, Texas, and West Virginia.

OSHA found approximately 128 serious safety-related violations in these 40 inspections.[9] The four most frequent subjects of citation were: 1) respiratory protection, 2) recordkeeping, 3) hazard communication, and 4) medical services and first aid. In general, older and smaller plants were noted to have more hazards than newer, larger facilities. OSHA also reported that conditions found in chemical operations were developed to protect the safety and health of workers from common hazards and not from rare catastrophic events.

NICS

The National Institute for Chemical Studies (NICS) was founded in 1985 by West Virginia business and labor leaders, public officials, environmentalists, academicians, and others to reduce the risks posed by chemical plant operations. The Safeguards Report prepared by NICS[3] was intended to serve as a step toward developing a community hazard assessment program for the Kanawha Valley in West Virginia, and was based on information gathered through a questionnaire sent by NICS to industries in the Valley. The aim of the report was to identify the major potential chemical accident hazards that existed in the Kanawha Valley community and to characterize how these risks were being managed. PEI extracted control/mitigation information concerning six plants from the NICS study for incorporation into the study data base.

RESULTS

Control Systems

The analysis of control systems used in industry for controlling accidental releases was based on information from 48 industrial facilities. Of the control system data base for this study, 88 percent was obtained from EPA Region 6 reports, 10 percent from the NICS Safeguards Report, and 2 percent from OSHA ChemSEP inspection reports. In addition to the control devices discussed previously in this paper, routine maintenance inspections of process equipment and monitor-activated automatic process shutdown mechanisms were also included as major control systems for this analysis.

Table I summarizes the specific types of accidental release control systems encountered in this review as a function of the type of chemical released. The most prevalent control devices used to handle accidental releases were flares and scrubbers. The most commonly reported control system (accounting for 40 percent of the total control system data base), however, was not specifically a control device but the implementation of routine maintenance inspections of the chemical process line. These routine maintenance inspections include visual inspections for leaks or corrosion in piping and reactors, as well as manual checks on process equipment such as valves, compressors, and pumps.

A few special types of accidental release control systems were also found in the data base. One company had installed a chlorine vaporizing apparatus so that any released chlorine could be emitted more safely as a vapor than as a liquid. Another plant had implemented X-ray and ultrasound techniques to detect early signs of equipment failure. A third plant listed a thermal oxidizer as a control device. This may have been a flare or an incinerator but, in the absence of such details, the thermal oxidizer is listed in Table I under the "other control systems" category.

With respect to the types of chemicals handled or processed, no major control system usage trends could be discerned because of the limited control data available per chemical. A variety of control systems were reported for methyl chloride and vinyl chloride, the two chemicals with the maximum amount of control-related data. Flares appear to be the preferred accidental release control devices for hydrogen sulfide and hydrogen cyanide.

Table II analyzes the same control systems by type of facility. Four types of facilities were delineated from the data base: 1) fertilizer manufacturing, 2) industrial chemical manufacturing, 3) petrochemical refining, and 4) polymer/synthetic fiber manufacturing. Because of limited information in the data base, the type of facility could not be distinguished for 23 of the 48 cases studied in this analysis. The predominant type of facility in the control system data base was industrial chemical manufacturing. A variety of control systems are employed in this type of facility. No major trends for control systems by type of facility were readily apparent from the data analysis because of the limited data available per facility category.

The data base also revealed some information on problems associated with control devices. In two cases involving accidental releases of hydrogen sulfide, the pilot flame to the flare systems at the plants had been extinguished accidentally. It was further reported that the flare ignitor had been poorly maintained at one site. At another site, an accidental release was attributed to an automatic pressure controller located too close to a process valve, thereby causing the transient pressure fluxes from the valve to open the controller prematurely. Four sites reported problems with control system operation due to loss of power at the plant (e.g., bypass of scrubber, shutdown of incinerator).

TABLE I. CONTROL SYSTEMS FOR ACCIDENTAL RELEASES BY TYPE OF CHEMICAL

Chemical	Flare	Incinerator	Scrubber	Monitor-activated automatic shutdown	Maintenance checks	Other control systems	Total
Acrylonitrile	0	0	1	0	0	-	1
Ammonia	2	0	0	1	2	-	5
Chlorine	0	0	1	0	3	Chlorine vaporizer (1)	5
Cyclohexane	0	0	0	0	1	-	1
Ethylene dichloride	0	0	0	1	0	-	1
Ethylene oxide	0	0	1	1	3	-	5
Hydrogen cyanide	2	0	0	0	0	-	2
Hydrogen fluoride	0	0	1	0	0	-	1
Hydrogen sulfide	3	0	0	0	1	-	4
Methyl chloride	0	0	1	1	6	X-ray and ultrasound inspections (1), thermal oxidizer (1)	10
Methyl isocyanate	1	0	0	0	0	-	1
Phosgene	0	0	0	1	1	-	2
Sulfur dioxide	0	1	0	0	0	-	1
Vinyl chloride	1	3	3	0	2	-	9
Total	9	4	8	5	19	3	48

TABLE II. CONTROL SYSTEMS FOR ACCIDENTAL RELEASES BY TYPE OF FACILITY

Type of facility	Flare	Incinerator	Scrubber	Monitor-activated automatic shutdown	Maintenance checks	Other control systems	Total
Fertilizer manufacturer	0	0	0	0	2	-	2
Industrial chemical manufacturer	1	1	3	2	7	X-ray and ultra-sound inspections (1)	15
Petrochemical refinery	1	0	1	0	1	-	3
Polymer/synthetic fiber manufacturer	1	0	1	0	3	-	5
Total	3	1	5	2	13	1	25

During the review of the control system data base, some information was also found on control techniques for routine HAP emissions. This information indicates that incinerators are primarily used for HAP destruction under routine conditions. One plant, however, mentioned the use of a stripping tower for handling routine hydrogen cyanide emissions.

Mitigation Systems

The analysis of mitigation systems was based on data from 17 industrial sites. The mitigation system data base consisted of 15 incidents from EPA Region 6 reports and 2 from the NICS Safeguards Report.

Three major categories of mitigation systems were established from a review of the data base: 1) water misting or deluge system with waste sent to wastewater treatment via permanent dikes and trenches; 2) permanent dikes with vacuum truck removal of the volatile liquid spill; and 3) temporary, set-up containment barriers with vacuum truck removal of the volatile liquid spill. Table III summarizes the types of mitigation systems in use at industrial facilities as a function of the type of chemical released. In addition to the aforementioned major categories of mitigation systems, a few specific types of mitigation systems were also found in the data base. One plant uses an automatic caustic neutralization system which supplies caustic to react with the chlorine overflow from a scrubber control system. The liquid waste is contained by a permanent dike and then sent to the wastewater treatment system via trenches. Two other plants use foam suppressant covers to minimize surface emissions. The resulting covered liquid spill is then vacuumed by truck for disposal. A third plant had a special clamp fabricated to mitigate vinyl chloride emissions from a valve joint until permanent repairs could be made. Because of the limited data available per chemical in the mitigation system data base, no true trends could be established for mitigation systems by type of chemical. For the two facilities handling ammonia, water misting was reported as the mitigation system for accidental release of the chemical.

Preventive Measures

In addition to control and mitigation systems, the data base also provided information on preventive measures that industrial facilities use after an accidental release to prevent the recurrence of similar accidental releases. Of the 30 industrial sites constituting the preventive measures data base, 26 (87 percent) were obtained through a review of EPA Region 6 reports, whereas the other 4 (13 percent) were obtained from the NICS Safeguards Report.

Four major categories of prevention measures were identified: 1) improved inspection techniques and better equipment testing, 2) improved contingency plans for minimizing accidental release exposures, 3) improved operating procedures, and 4) improved design of process or control/mitigation

TABLE III. MITIGATION SYSTEMS FOR ACCIDENTAL RELEASES BY TYPE OF CHEMICAL

Chemical	Water mist or deluge to treatment	Permanent dikes/ vacuum removal	Temporary containment barriers/ vacuum removal	Other mitigation systems	Total
Ammonia	2	0	0	-	2
Benzene	0	0	1	-	1
Chlorine	1	0	0	Automatic caustic neutralization/diked to treatment (1)	2
Ethylene oxide	1	0	0	-	1
Hydrogen cyanide	0	0	0	Foam suppressant cover - vacuumed (1)	1
Hydrogen peroxide	0	0	0	Foam suppressant cover - vacuumed (1)	1
Methyl chloride	1	0	0	-	1
Naphtha	0	0	1	-	1
Propylene dichloride	0	0	1	-	1
Toluene	0	1	0	-	1
1,1,2-Trichloroethane	0	0	1	-	1
Trichloroethene	0	1	0	-	1
Vinyl chloride	1	0	0	Fabricated clamp to valve (1)	2
Xylene	0	1	0	-	1
Total	6	3	4	4	17

systems. Table IV identifies the preventive measures by type of chemical. Improved inspection techniques and equipment testing were reported in the data base as the most common preventive measure practiced in industry. Improved design of process or control/mitigation systems was also a common preventive measure. Under this category, three of the nine sites mentioned revamping the design of the existing accidental release control system. One of these three sites reported that their flare system used to handle hydrogen cyanide releases needed to be enlarged. At another site (handling hydrogen sulfide), a backup flare ignition system had to be installed to prevent flare outages. The third site was in the process of enlarging its vapor scrubber system to prevent direct chlorine venting in the event of primary equipment failure. Other preventive measures reported in the data base were the use of improved materials of construction, the installation of a flare as a control device for ethylene oxide, and the setting up of a foam suppressant system to mitigate hydrogen peroxide spills.

CONCLUSIONS

A review of the control/mitigation system data base developed during a study conducted by PEI for EPA reveals that the major control measure employed by industry for accidental releases is routine process inspections. With respect to control devices, flares and scrubbers were found to be the control systems of choice for handling such releases. The types of accidental release control systems appear to be chemical-specific although insufficient data were available per chemical to establish trends for different chemicals. In the case of hydrogen sulfide and hydrogen cyanide, flares seem to be the preferred control device in industry for accidental releases. The mitigation systems data base revealed a variety of techniques (e.g., water misting, dikes, foam covers) in industry for limiting the spread of an accidental release. The limited data base did not allow any clear trends to be established for mitigation systems by type of chemical. The control/mitigation system data base also pointed out that companies viewed improved inspections and equipment testing as the best way of preventing accidental releases.

Although extensive information is currently available from EPA data bases (e.g., AHE) on the general characteristics of accidental releases (e.g., quantities released, causes, and end effects of the release), very limited information is available on control/mitigation systems associated with accidental releases. Under Section 305(b) of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA), EPA has initiated a review of emergency systems designed to monitor, detect, and prevent accidental chemical releases.[7] One of the goals of this review is to clarify relationships between facility characteristics, emergency system characteristics, and system effectiveness. This review should provide additional information to industry on control strategies for accidental releases.

TABLE IV. PREVENTIVE MEASURES FOR ACCIDENTAL RELEASES BY TYPE OF CHEMICAL

Chemical	Improved inspections and equipment testing	Improved contingency plans	Improved operating procedures	Improved design of process or control/ mitigation systems	Other preventive measures	Total
Acrylonitrile	1	0	0	0	-	1
Ammonia	3	1	0	1	-	5
Chlorine	1	0	1	1	-	3
Cyclohexane	0	1	0	0	-	1
Ethylene dichloride	0	0	0	1	-	1
Ethylene oxide	2	0	0	0	Flare installation (1)	3
Hydrofluoric acid	0	1	0	0	-	1
Hydrogen cyanide	0	0	0	2	-	2
Hydrogen peroxide	0	0	0	0	Installation of foam suppressant system (1)	1
Hydrogen sulfide	0	0	0	1	-	1
Methyl chloride	3	1	0	2	Improved materials of construction (1)	7
Phosgene	1	0	1	0		2
Toluene	0	0	0	1	-	1
Vinyl chloride	1	0	0	0	-	1
Total	12	4	2	9	3	30

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